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(12) **EUROPEAN PATENT APPLICATION**

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(54) Chemical sensor.

(57) A chemical sensor for detecting at least one gas component in a gas sample, and comprising at least one vibrating member coated with a reactive material which selectively interacts with said gas component thus increasing the coating's mass and reducing the natural resonance frequency of said vibrating member ;

According to this invention, the vibrating member consists of a cantilevered beam (10) suspended from a support (14) and carrying a layer (30) of reactive material, said beam being vibrated at its natural resonance frequency by an oscillator (34) and being further coupled to a sensor means (20) for generating a signal having a frequency component equal to the vibration frequency of said beam.
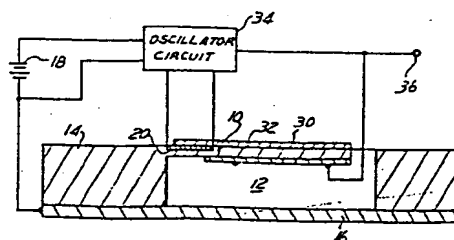
For use in the analyze of gas samples.

FIG.2

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CHEMICAL SENSOR

The present invention is related to the field of solid state chemical sensors, and in particular to such sensors which are used for detecting a gas component in a gas sample and comprise at least one vibrating member coated with a reactive material which selectively inter-

5   acts with said gas component thus causing a change in the coating's mass and consequently in the natural resonance frequency of the vibrating member.

Solid state chemical sensors in which changes in conductivity of a material are produced in response to the reaction and/or absorption

10   of a specific gas are known in the art. Typical of these sensors are the adsorption field effect transistor (ADFET) as disclosed in U.S. Patent No. 3 831 432, the thin film semiconductor NO_x sensor as disclosed in U.S. Patent No. 4 169 369, the titania oxygen sensor disclosed in U.S. Patent No. 4 007 435, and the palladium hydrogen sensor taught by U.S.

15   Patent No. 3 242 717. Another type of solid state chemical sensor is the coated piezoelectric crystal sensor as disclosed in U.S. Patents Nos. 3 164 004, 3 260 104, 3 744 296 and 3 828 607. In these sensors a piezoelectric crystal is coated with a material which selectively inter- acts with a given gas component causing a change in the coating's mass

20   and the natural resonance frequency of the coated crystal. An electronic crystal oscillator circuit vibrates the coated crystal at its resonance frequency producing an output signal having a frequency indicative of the quantity of the gas component that has interacted with the coating.

It is an essential object of the present invention to provide

25   a chemical sensor of the coated vibrating member type which has an in- creased sensitivity over the sensors of the prior art.

This object is achieved, according to the teaching of the invention, and in a chemical sensor of the kind referred to above, thanks to the fact that the vibrating member consists of a beam suspended for

30   vibration from a support structure and carrying on at least one surface thereof a layer of reactive material, said beam being vibrated at its natural resonance frequency by an oscillator and being further associated with

sensor means for detecting its vibration to generate a resonance frequency
signal having a frequency component equal to the vibration frequency of
said beam.   Advantageously, this resonance frequency signal is amplified
in the oscillator to generate an output signal which itself is delivered

5   to means for producing a force on the beam to sustain its vibration at
its resonance frequency.

One advantage of the disclosed chemical sensor is that the
change in the natural resonance frequency of the cantilevered beam is
inversely proportional to the mass of the gas component which interacted

10   with the reactive chemically modified surface.   Another advantage is that
cantilevered beam structure and supporting electronic circuitry may be
contained on a single semiconductor chip.   Another advantage is that the
complete structure and supporting electronic circuits can be fabricated
using existing semi-conductor and integrated circuit technology.   Another

15   advantage is that the sensor may include a plurality of cantilevered
beams, each beam being sensitized with a reactive material responsive to
a different gas component, or alternatively, the sensor possibly inclu-
ding a reference cantilever beam and an electronic circuit for generat-
ing a reference signal.   Another advantage is that the supporting elec-

20   tronics fabricated on the single semiconductor chip may include mixer
circuits for generating signals having a frequency indicative of the
change in the natural resonance frequency of each beam having a sensi-
tized surface due to the added mass resulting from a chemical reaction
or absorption.

25   These and other advantageous features of the invention will
become readily apparent from reading the following description of some
preferred embodiments, given by way of examples only, and with reference
to the accompanying drawings, in which :

- Figure 1 is a top view of a chemical sensor according to

30   the invention ;

- Figure 2 is a cross-sectional view along line 2-2 of the
sensor shown in Figure 1 ;

- Figure 3 is a top view of an alternate embodiment of the
chemical sensor according to the invention ;

35   - Figure 4 is a cross-sectional view along line 4-4 of the
embodiment shown in Figure 3 ;

- Figure 5 is a partial top view of the sensor showing an
interdigital heater element disposed on the upper surface of the canti-

levered beam ;

   - Figure 6 is a top view of a dual beam sensor according to the invention ; and

   - Figure 7 is a top view of a multiple beam sensor.

   Referring to Figures 1 and 2, there is shown a top and cross-sectional view of the chemical sensor. A thin silicon or silicon dioxide cantilever beam 10 is suspended over an etched well 12 formed in a silicon substrate 14. The silicon substrate 14 is attached to a conductive base element 16. The base element 16 may be a metal plate as illustrated in Figure 2 or alternatively may be a silicon or quartz plate having a conductive metal electrode 17 disposed on its surface adjacent to the cantilever beam 10 (see Fig. 4).

   A stress sensor such as piezoresistive bridge 20 is disposed on the beam adjacent to its cantilevered or base end. The individual piezoresistive elements of the bridge 20 can be either diffused or ion-implanted on the silicon surface using techniques well known in the art. The four corners of the piezoresistive bridge are connected to terminals 22, 24, 26 and 28. The bridge 20 is energized by a source of electrical power, illustrated as battery 18 applying a potential difference between terminals 26 and 28, and generates an output signal between terminals 22 and 24 having a frequency component corresponding to the vibration frequency of beam 10.

   The upper surface of beam 10 is sensitized with a layer of reactive material 30 which may chemically react with or absorb a specific component of the gas to be analyzed in a reversible or irreversible mode. Alternatively, the entire surface of the beam 10 may be sensitized with a layer of reactive material 30, increasing the detectivity of the sensor.

   The output terminals 22 and 24 of the bridge 20 are connected to the inputs of an oscillator circuit 34 which also receives electrical power from battery 18. The output of the oscillator circuit 34 is connected to an output terminal 36 and to an electrode 32 disposed on the bottom side of cantilever beam 10 adjacent to the conductive base element 16. In the preferred embodiment, the oscillator circuit 34 is formed directly on the surface of substrate 14 using conventional integrated circuit technology.

   In operation, the piezoresistive bridge 20 generates an oscillating signal having a frequency corresponding to the frequency of the vibrating cantilever beam 10. This output signal is received by the

oscillator circuit 34 which generates an output signal applied to elec-
trode 32.   The output signal applied to electrode 32 generates an oscil-
lating electric field between the cantilever beam 10 and the base plate
16, and produces an electrostatic force on beam 10.   It is assumed that
the oscillator circuit 34 has the requisite phase shift capabilities
such that the generated electrostatic force sustains the vibration of
the beam 10 at its natural resonance frequency.   The cantilever beam 10
is equivalent to the tuned circuit of a Hartley or Colpitts oscillator
or the piezoelectric crystal in a Pierce type oscillator.

         The fundamental resonance frequency of the cantilever beam
is given by :

$$f = 0,16 \ (E/\rho)^{\frac{1}{2}} \ (t/L^2) \hspace{3cm} (1)$$

where :

E is Youngs Modulus for silicon

ρ is the density of silicon

t is the beam's thickness, and

L is the beam's length

         In a typical embodiment of the sensor in which t = 35 μ m
and L = 350 μ m, the resonance frequency "f" of beam 10 would be 320 kHz.

         Upon exposure of the sensor to a gas sample to be analyzed
containing the specific component to which the layer of reactive mate-
rial 30 interacts, the specific gas will either chemically react with
layer 30 or be absorbed by the layer.   The term "interact" as used here-
inafter will mean either a chemical reaction or an absorption of the
specific component with the reactive material or both.   This interacted
gas increases the mass of the beam 10.

         In accordance with the teachings of Sauerbrey in Z.   Phys.
178,457 (1964), the change in the resonance frequency of the beam, Δf,
due to the added mass, Δm, of the interacted gas component is :

$$\Delta f/f = -\Delta m/tA\rho \hspace{3cm} (2)$$

where A is the coated surface area and f, t and ρ are as defined for
equation (1).   The mass sensitivity of the sensor where the beam thick-
ness t = 35 μ m, the beam length L = 350 μ m and the beam width w = 100 μ m,
is approximately 113 kHz per microgram of the interacted component.   The
quantity Δm of the interacted component may, therefore, be determined
directly from the change in the resonance frequency of the cantilevered
beam 10.

Referring now to Figures 3 and 4, there is shown an alternate embodiment of the chemical sensor. Elements common to both embodiments of the sensor have the same reference numerals. In the embodiment of Figures 3 and 4, the strain sensor 20 comprises serially connected piezo-

5   resistive elements 50 and 52 forming a voltage divider. Piezoresistive element 50 is disposed on the top surface of cantilevered beam 10 while piezoresistive element 52 is disposed on the top surface of the silicon substrate 14. As with the piezoresistive bridge the elements 50 and 52 may be formed directly on the surfaces of silicon substrate and beam

10   using diffusion or ion-implantation techniques. A potential difference from a source of electrical power, such as battery 18 connected between terminals 54 and 56, is applied across serially connected piezoresistive elements 50 and 52. The resistance of piezoresistive element 50 changes with the vibration of beam 10 producing an oscillating signal at junction

15   58 having a frequency corresponding to the vibration frequency of beam 10. The signal at junction 58 is input to an oscillator circuit 34 which generates an output signal applied to electrode 32 disposed on the bottom surface of beam 10. As previously described, the output signal applied to electrode 32 generates an oscillating electric field between the canti-

20   levered beam 10 and the thin film electrode on base plate 16 producing an electrostatic force sustaining the vibration of beam 10 at its natural resonance frequency. The output of the oscillator circuit 34 is also communicated to an output terminal 36. As in the embodiment of Figures 1 and 2, the oscillator circuit 34 may be formed directly on the surface

25   of the silicon substrate 14 or may be a separate entity.

The embodiment shown on Figures 3 and 4 further includes a heater element 40 disposed on the upper surface of beam 10. The layer of reactive material 30 is disposed over the heater element 40. The heater element allows the beam to be heated to drive off the absorbed

30   gas molecules thereby regenerating the sensor. Alternatively, the heater may be used to heat the layer of reactive material to a temperature optimizing the interaction between the reactive material and the selected component of the gas to be analyzed. This capability is very advantageous when the sensor is operated in a cold environment where the reaction and/

35   or absorbtion process of the reactive material may be substantially retarded.

The heater element 40 may be a thin layer of resistive mate-
rial, such as tin oxide, deposited between a pair of parallel electrodes
42 and 46 as shown on Figure 3. Electrical power is applied to the heat-
er element via terminals 44 and 48 connected to electrodes 42 and 46,
5   respectively.

Alternatively, the heater element 40 may be an interdigital
resistive element 60 disposed on the upper surface of beam 10 as shown
in Figure 5. As in the embodiment illustrated in Figure 3, electrical
power to heater element 60 is applied through conductor electrodes 42
10   and 46. The layer of reactive material 30 is omitted from Figure 5 to
simplify the drawing.

Referring now to Figure 6, there is shown another embodiment
of the chemical sensor having two cantilevered beams of the type described
with reference to Figures 1 through 4. The physical dimensions of the
15   two beams are selected so that they both have the same natural resonance
frequency. In this embodiment, only beam 110 has a layer of reactive
material 30 which interacts with a selected component of the gas to be
analyzed. The other beam 112 does not have a layer of reactive material
and functions as a reference signal generator. Both beams 110 and 112
20   have an associated strain sensor 120 and 122, respectively, disposed on
their upper surfaces adjacent to the cantilevered supported ends. These
strain sensors may be a piezoresistive bridge as described with reference
to Figure 1, a piezoresistive voltage divider as illustrated on Figure 3,
or a single piezoelectric element.

25   The output of strain sensor 120 associated with the first
beam 110 is received by a first oscillator circuit 134 which generates
an output which is connected to the electrode on the bottom of beam 110
by means of a lead 136.

Similarly, the output of strain sensor 122 is received by a
30   second oscillator circuit 144 which generates an output which is connec-
ted to the electrode on the bottom of beam 112 by means of a lead 146.

The outputs of the first oscillator circuit 134 and second
oscillator circuit 144 are also received by a mixer circuit 150 of con-
ventional design. The mixer circuit 150 mixes the two received output
35   signals and generates a difference signal on terminal 152 having a fre-
quency component equal to the difference between the frequency of the
signal received from the first oscillator circuit and the frequency of
the signal received from the second oscillator circuit.

As the layer of reactive material 30 on the surface of beam 110 reacts with the selected component of the gas sample, when present, a change Δm in the mass of the beam is provided. In accordance with equation (2) the resonance frequency of beam 110 will change inversely proportionate to the change in the mass Δm. The frequencies of the signals produced by the first and second oscillator circuits will now be different and the signal from mixer circuit 150 will have a frequency proportional to the quantity or mass of the interacted component of the gas sample.

The dual beam arrangement of the sensor of Figure 6 has the advantage that it is relatively insensitive to temperature, pressure or attitude with respect to gravity since these factors will affect both beams alike and the frequency difference of the signal generated by the mixer circuit 150 will remain proportional to the quantity of component which interacted with the reactive material disposed on the surface of beam 110.

The dual beam arrangement of Figure 6 also permits the isolation of a specific gas component when the reactive material disposed on beam 110 may also be sensitive to a second gas component such as water or carbon dioxide. To isolate the frequency response of beam 110 to only the frequency change caused by the interaction of the specific gas component the beam 112 may include a layer of reactive material responsive to water and/or carbon dioxide only, such that the change in resonance frequencies of beams 110 and 112 due to the presence of water and/or carbon dioxide in the sample will be the same. Therefore, the frequency difference output by mixer circuit 150 will be proportional only to the quantity of the specific gas component which interacts with, or is absorbed by the reactive layer on beam 110, independent of the quantity of water or carbon dioxide in the sample.

Referring now to Figure 7, there is shown a multibeam embodiment of the chemical sensor. The sensor has a plurality of cantilevered silicon beams 110 through 118 suspended over a well formed in a silicon substrate. The structure of each individual beam is equivalent to the structures shown on Figures 1 through 4, each beam having an associated strain sensor and an associated oscillator circuit. For illustrative purposes it is assumed that beam 112 has no layer of reactive material and in conjunction with its associated strain sensor 122 and oscillator circuit 144 functions as reference signal generator. Beam 110 is sensi-

tized with a first reactive material responsive to a gas component A,
and has a strain sensor 120 and an associated oscillator circuit 134.
Beam 114 is sensitized with a second reactive material responsive to a
gas component B, and has a strain sensor 124 and an associated oscillator
circuit 154. Beam 116 is sensitized with a third reactive material res-
ponsive to a gas component C and has a strain sensor 126 and an associated
oscillator circuit 164. Beam 118 is sensitized with a fourth reactive
material responsive to gas components C and D.

The outputs of oscillator circuits 134 and 144 are received
by a mixer circuit 150 which generates a signal having a frequency pro-
portional to the quantity of gas component A. The outputs of oscillator
circuits 144 and 154 are received by a mixer circuit 160 which generates
a signal having a frequency proportional to the quantity of gas compo-
nent B. Similarly, the outputs of oscillator circuits 144 and 164 are
received by a mixer circuit 170 which generates a signal having a fre-
quency proportional to the quantity of gas component C. In an equivalent
manner, the outputs of oscillator circuits 164 and 174 are received by a
mixer circuit 182 which generates a signal having a frequency proportional
to gas component D.

The frequency signals generated by mixer circuits 150, 160,
170 and 180 may be input into a storage device 190 where they are stored
or may be input to a display device 200 calibrated to produce a visual
display indicative of the quantities of the selected gases A, B, C and D
that have been reacted with or absorbed by the reactive materials on the
associated beams. The storage device 190 may be a solid state memory
storing digital words indicative of the frequencies of the received sig-
nals or a magnetic tape storing the frequencies directly. The display
device 200 may be a cathode ray tube, or any solid state visual display
panel such as a LED or liquid crystal display pannel.

Various types of reactive materials which are capable of
interacting with one or more components of a gas to be analyzed are known
in the art. As reported by J. Hlavay and G.G. Gullbault, in their article
"Applications of the Piezoelectric Crystal Detector in Analytical Chemistry"
Analytical Chemistry, Vol. 49, No. 13, November 1977, pp. 1890-1898,
S_iO_x coatings may be used to detect water, triethanolamine quadrol to
detect SO_2, $FeCl_3$ to detect diisopropylmethyl phosphonate (pesticides)
and Ascorbic Acid with silver acid to detect ammonia. This article
discloses many other coatings which may be used as a reactive surface

applied to the surfaces of beam 10. Other types of reactive coatings have been disclosed in U.S. Patents Nos. 3 164 004, 3 260 104, 3 266 291 and 3 744 296.

These coatings may be applied or deposited on the surface of
5 the beam 10 by any physical means such as spraying, painting, dipping, ion implantation or vapor deposition. However, it is preferred that when possible the coating be chemically bonded to the beam's surface. This produces a more rugged sensor. Chemical bonding can be accomplished by reacting the coating chemical with active molecular or atomic groups
10 on the surface of the beam. As previously indicated the layer of reactive material 30 may be formed only on the top surface of beam 10 as shown in Figures 1 and 2. However, the sensitivity of the sensor may be increased by sensitizing the entire surface of the beam.

Although the invention has been disclosed using specific
15 materials and configuration of the vibrating beam chemical sensor, it is not intended that the scope of invention be limited to the embodiments illustrated and described.

CLAIMS

1. A chemical sensor for detecting at least one gas component in a gas sample, and comprising at least one vibrating member coated with a reactive material which selectively interacts with said gas component thus causing a change in the coating's mass and consequently in the natural resonance frequency of said vibrating member, characterized in that the vibrating member consists of a beam (10) suspended for vibration from a support structure (14) and carrying on at least one surface thereof a layer (30) of reactive material, said beam being vibrated at its natural resonance frequency by an oscillator (34) and being further associated with sensor means (20) for detecting its vibration to generate a resonance frequency signal having a frequency component equal to the vibration frequency of said beam.

2. A chemical sensor according to claim 1, characterized in that the resonance frequency signal is amplified in the oscillator (34) to generate an output signal which itself is delivered to means (16, 32) for producing a force on the beam (10) to sustain its vibration at its resonance frequency.

3. A chemical sensor according to claim 2, characterized in that the means for producing a force comprises a first electrode (32) disposed on one surface of the beam (10) and a second electrode (16) fixedly carried by the support structure (14) proximate said first electrode, said output signal being applied between said first and second electrodes to generate an oscillating electrostatic field therebetween which produces an oscillating electrostatic force on the beam (10) sustaining the vibration thereof.

4. A chemical sensor according to any of claims 1-3, characterized in that the beam (10) is a cantilevered beam having a base end fixedly attached to a supporting substrate (14) and an opposite free end.

5. A chemical sensor according to claim 4, characterized in that said supporting substrate (14) and cantilevered beam (10) are an integral structure.

6. A chemical sensor according to claim 5, characterized in that the material of said integral structure (10, 14) is a semiconductor material.

7. A chemical sensor according to any of claims 1 to 6, characterized in that it further includes heater means (40) disposed on the surface of the beam (10) for heating said layer (30) of reactive material.

8. A chemical sensor according to any of claims 4 to 7, characterized in that said supporting substrate (14) has a thickness greater than the thickness of the beam (10) and has an aperture (12) passing therethrough, and in that the cantilevered beam is suspended over one end of said aperture.

9. A chemical sensor according to claim 8, characterized in that said second electrode (16) is a metal plate covering the opposite end of said aperture (12).

10. A chemical sensor according to any of claims 5 to 9, characterized in that said sensor means (20) and oscillator (34) are formed directly on the surface of said integral structure (10, 14).

11. A chemical sensor according to claim 10, characterized in that said sensor means (20) is a piezoresistive bridge formed at the base end of the beam (10) adjacent to said integral structure (14).

12. A chemical sensor according to claim 10, characterized in that said sensor means (20) is a dual element voltage divider (50, 52) having at least one piezoresistive element (50) disposed at the base end of the beam (10) adjacent to said integral structure (14).

13. A chemical sensor according to any of claims 1 to 12, characterized in that it includes two beams (110, 112) having the same initial resonance frequency and each associated with a respective oscillator (134, 144) and a respective sensor means (120, 122), at least one (110) of said beams carrying a layer (30) of reactive material, and a mixer circuit (150) responsive to the resonance frequencies of said two beams (110, 112) to generate an output signal having a frequency component equal to the difference between their resonance frequencies.

14. A chemical sensor according to claim 13, characterized in that said two beams (110, 112) carry layers of different reactive materials.

15. A chemical sensor according to claim 14, characterized in that the layer of reactive material carried one one of said two beams (110, 112) interacts with a first and a second component of the gas sample to be analyzed, and the layer of reactive material carried on the other beam interacts with only said first component of the gas sample.

16. A chemical sensor according to any of claims 1 to 12, characterized in that it includes a plurality of beams (110, 112, 114, 116, 118) carrying layers of reactive materials which interact with different components of the gas sample to be analyzed, each beam being

associated with a respective oscillator (134, 144, 154, 164, 174) and a respective sensor means (120, 122, 124, 126, 128).

17. A chemical sensor according to claim 16, characterized in that it further includes a reference beam (112) carrying no layer of reactive material, said reference beam being associated with a reference oscillator (144) and a reference sensor means (122).

18. A chemical sensor according to claim 17, characterized in that it further includes mixer circuits (150, 160, 170, 180) responsive to the resonance frequencies of each of said beams (110, 114, 116, 118) and said reference beam (112) to generate an output signal for each beam, each output signal having a frequency component equal to the difference between the resonance frequency of its associated beam and the resonance frequency of the reference beam.

19. A chemical sensor according to claim 18, characterized in that at least one (118) of said beams carries a layer of reactive material interacting with two different components of the gas sample to be analyzed and a second (116) of said beams carries a layer of reactive material responsive to only one of said two different components, and in that the sensor further includes a mixer circuit (180) for generating an output signal in response to the resonance frequencies of said one and second beams (118, 116) having a frequency component equal to the difference between their resonance frequencies.

20. A chemical sensor according to claim 18 or 19, characterized in that said associated oscillator and sensor means and said reference oscillator and sensor means each generate an output signal indicative of the resonance frequencies of their associated beams and the reference beam respectively, and in that said mixer circuits are responsive to the output signals generated by said oscillator and sensor means.
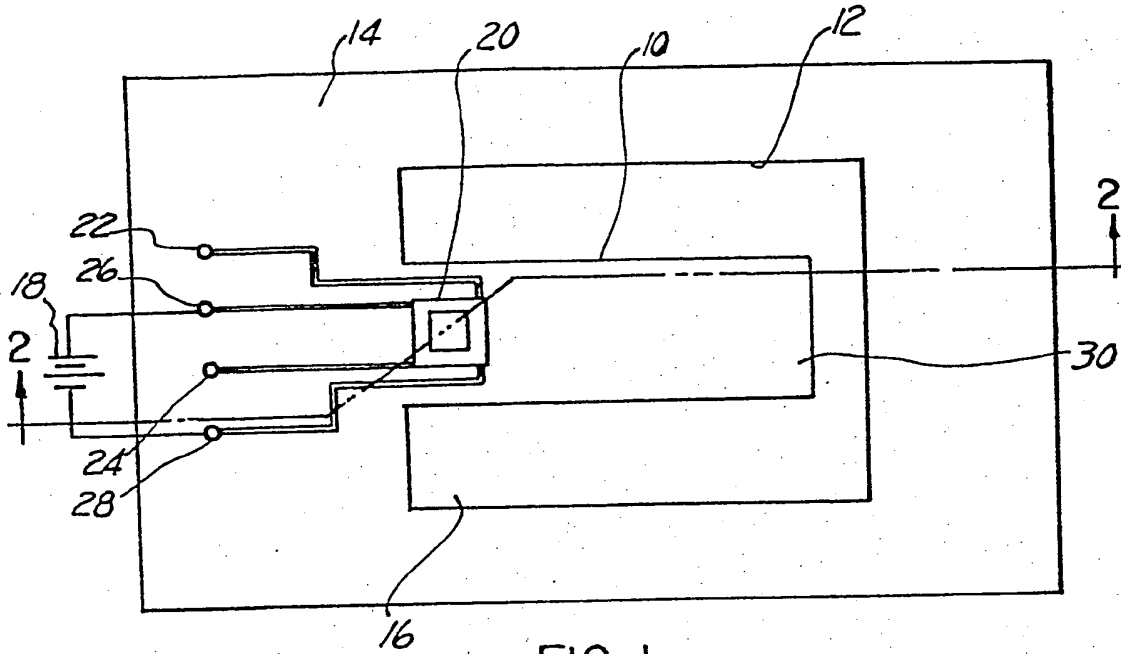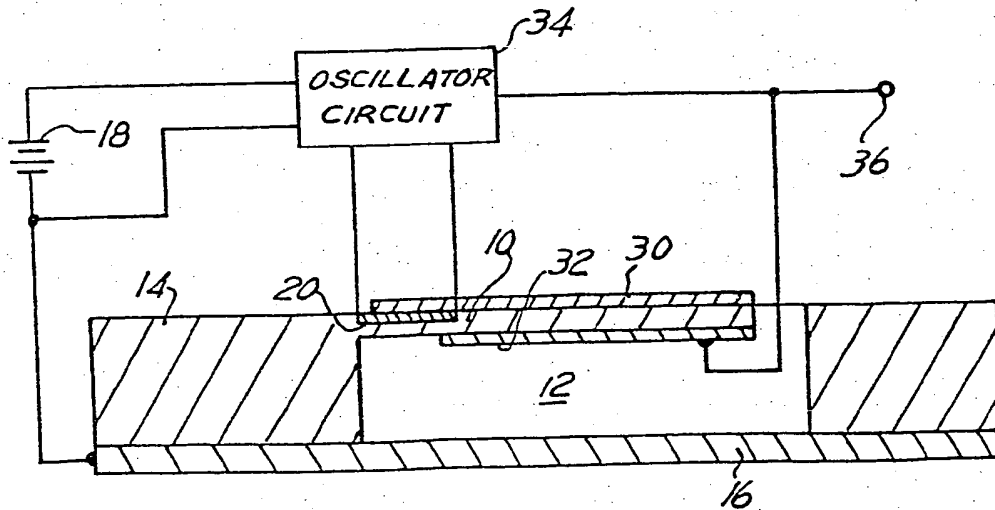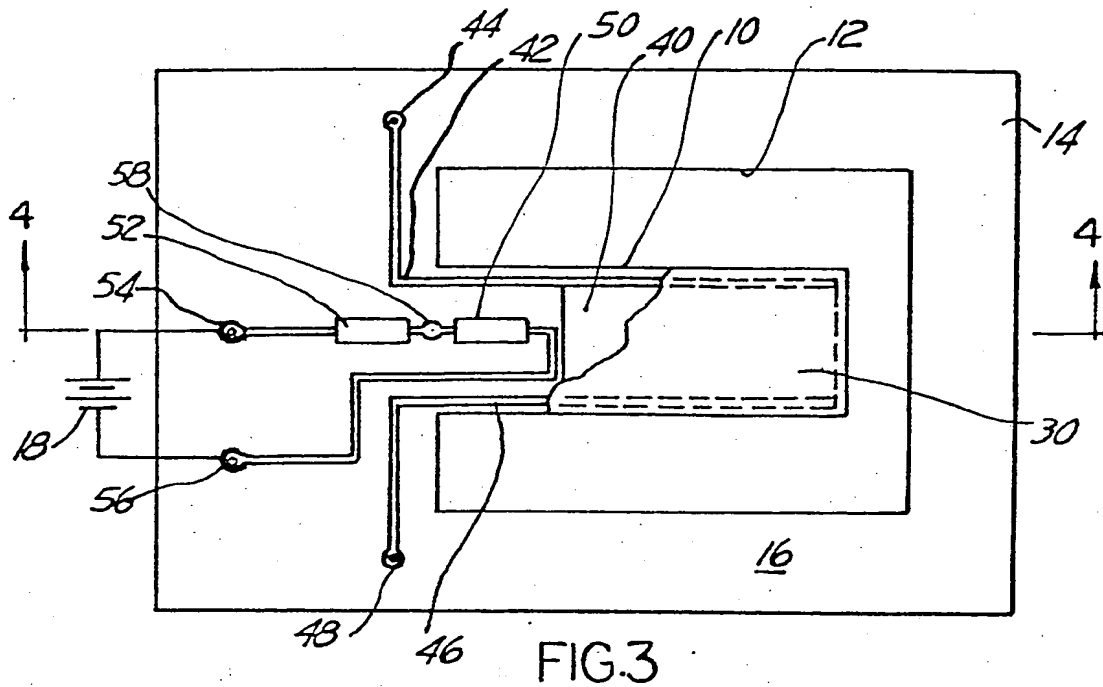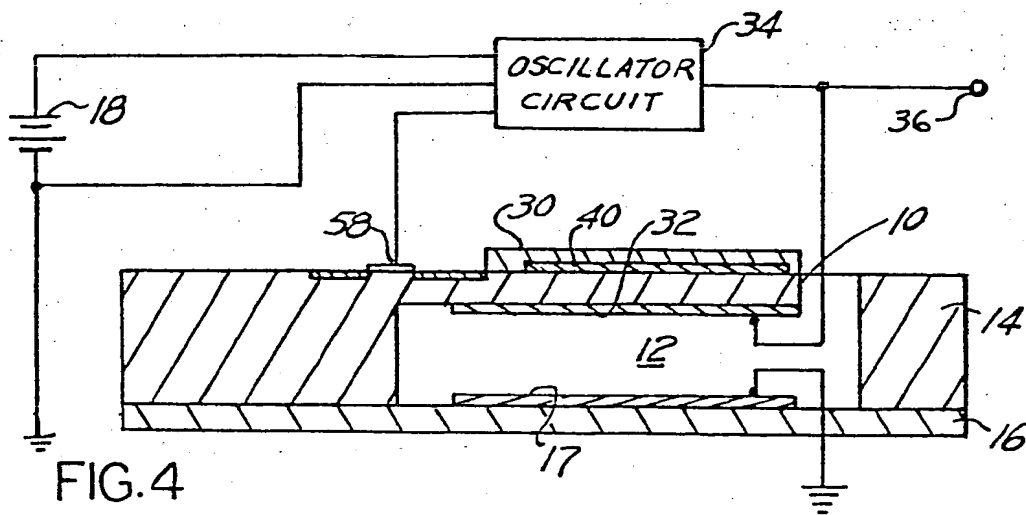
FIG. I

FIG.2

FIG.3

OSCILLATOR CIRCUIT

FIG.4

FIG.5

0072744

FIG.6

SECOND OSC. CIRCUIT

FIRST OSC. CIRCUIT

MIXER CIRCUIT

30
14
110
120
134
136
112
122
144
146
150
152

FIG.7

OSC. CIRCUIT

MIXER CIRCUIT

STORAGE DEVICE

DISPLAY DEVICE

110 112 114 116 118
120 122 124 126 128
134 144 154 164 174
150 160 170 180
190 200